



# The effects of sintering temperature of $\text{MnCr}_2\text{O}_4$ nanocomposite on the $\text{NO}_2$ sensing property for YSZ-based potentiometric sensor

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## ABSTRACT

In this paper,  $\text{MnCr}_2\text{O}_4$  with spinel structure has been prepared by using polymeric precursor method. The thermal stability, grain size and surface morphology of  $\text{MnCr}_2\text{O}_4$  calcined at different temperatures were studied using thermogravimetric analysis and differential scanning calorimeter analysis (TG-DSC), X-ray diffraction (XRD), scanning electron microscopy (SEM). Then the YSZ-based sensors using  $\text{MnCr}_2\text{O}_4$  sintered at different temperatures (800, 900, 1000, 1100 and 1250 °C) as electrode were fabricated and their  $\text{NO}_2$  sensing properties were investigated. Results demonstrate that  $\text{MnCr}_2\text{O}_4$  sample calcined at 1000 °C exhibits higher response to 100 ppm  $\text{NO}_2$ , which is about 73 mV. It is believed that the calcined temperature affect the material's sensing properties. In addition, the sensing characteristics such as selectivity, repeatability were investigated.

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## 1. Introduction

Lots of nitrogen oxide ( $\text{NO}$ ,  $\text{NO}_2$  and  $\text{N}_2\text{O}$ ) from fossil fuel combustion have been a major pollutant, which caused environmental problems such as photochemical smog, acid rain, ozone depletion and greenhouse effects. To detect the  $\text{NO}_x$  in environment, the high performance  $\text{NO}_x$  sensor has been urgently desired. The  $\text{NO}_x$  sensors using yttria-stabilized zirconia (YSZ) as oxygen-ion-conducting electrolyte have been widely reported [1–7].

YSZ-based potentiometric sensors are operated by measurement of the open-circuit potential (OCP) between two dissimilar electrodes, generally, in which Pt as reference and metal oxide as sensing electrodes. The different reaction kinetics on the two electrodes result in a measurable potential difference which is correlated to the gas composition as well as concentration [8]. Many studies focused on sensing electrode materials, device structure and sensing mechanism [9–28]. Lots of metal oxide and mixed-oxide have been investigated in YSZ-based potentiometric sensors in some early researches. N. Miura et al. reported that  $\text{ZnCr}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{NiO}$  and  $\text{Cr}_2\text{O}_3 + \text{NiO}$  could give good sensing properties to  $\text{NO}_2$  at elevated temperature [29–36]. P. Dutta et al. also examined that  $\text{Cr}_2\text{O}_3$  was an excellent sensing electrode [37]. E.

Bartolomeo et al. reported that  $\text{WO}_3$ ,  $\text{LaFeO}_3$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$  showed good sensing performance [38]. Girish M. Kale et al. developed  $\text{CuO} + \text{CuCr}_2\text{O}_4$  sensing electrode [39]. Also, the morphology of sensing electrode (SE) and sintering temperature of SE were found to be main factors of the  $\text{NO}_2$  sensitivity [36,40–42].

In this work, we synthesized Mn/Cr mixed-oxides for YSZ-based potentiometric sensors, which were tested about  $\text{NO}_2$  sensing property. The effects of annealing temperature on the particle size and  $\text{NO}_2$ -sensing property of  $\text{MnCr}_2\text{O}_4$  nanocomposite were investigated.

## 2. Experimental

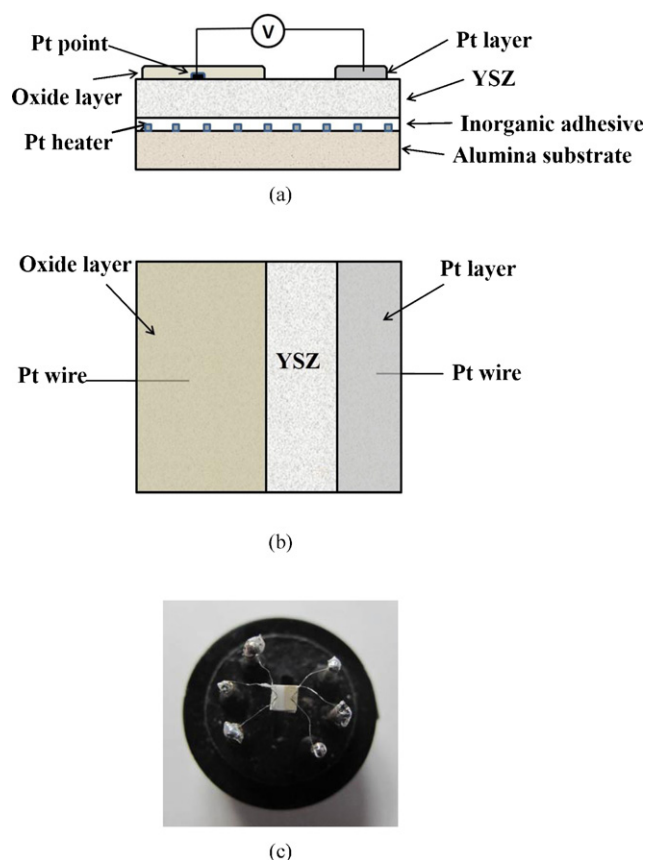
### 2.1. Materials preparation

$\text{MnCr}_2\text{O}_4$  was prepared from their nitrates by the polymer precursor method. In a typical synthesis process, citric acid and stoichiometric amounts of manganous acetate hydrate ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) and chromium (III) nitrate hydrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) were dissolved in deionized water, in which the molar ratio between citric acid and all the metal cations (Mn and Cr) was 3:1 with stirring at 70 °C for 2 h. Then ethylene glycol was added to the above solution with the citric acid/ethylene glycol mass proportion of 6:4. The resulted solution was maintained at 70 °C for 4 h at tube furnace, and sintered at 800, 900, 1000, 1100 and 1250 °C for 2 h in Muffle furnace after being grinded simply.

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**Scheme 1.** Schematic top view (a), cross-sectional view (b) of the planar sensor and the photo of the device (c).

## 2.2. Material characterization

Thermogravimetric analysis and differential scanning calorimetry analysis (TG-DSC, Netzsch, STA449 F3 Jupiter) were performed in air from 30–1300 °C at a heating rate of 10 °C/min to determine the thermal behaviors of the obtained gel. X-ray diffraction (XRD) patterns were obtained with Rigaku wide-angle X-ray diffractometer (D/max rA, using Cu K $\alpha$  radiation at wavelength  $\lambda=0.1541$  nm.). The XRD data were identified by comparison with the reference data from International Center for Diffraction Data (ICDD) files. The specific surface area was measured at 77 K with a Gemini VII and estimated by the Brunauer–Emmett–Teller (BET) method. Field-emission scanning electron microscopy (FESEM) observations of surface morphology of the sensing electrodes were carried out using a JEOL JSM-7500F microscope with an accelerating voltage of 15 kV.

## 2.3. Fabrication and measurement of sensors

As shown in Scheme 1, the sensor was fabricated using YSZ plate (8 mol% Y<sub>2</sub>O<sub>3</sub>-doped, 2 × 2 mm, 0.2 mm thickness, provided by Tosoh Corp., Japan.). A point-shaped and a narrow stripe-shaped Pt electrode were formed on the two ends of the as-corroded YSZ plate by applying the commercial Pt paste (Sino-platinum Metals CO., Ltd.). The prepared oxide material (the MnCr<sub>2</sub>O<sub>4</sub> sintered at 800, 900, 1000, 1100 and 1250 °C) was mixed with pure water, and applied on the point-shaped Pt electrode with brush as the sensing electrode, followed by sintering at 800 °C for 2 h. The thickness of the electrode is approximately 200  $\mu$ m. Then, a Pt heater formed on Al<sub>2</sub>O<sub>3</sub> substrate was attached to the sensor device by chemical glue. The devices using MnCr<sub>2</sub>O<sub>4</sub> sintered at 800, 900, 1000, 1100

and 1250 °C as sensing electrode were fabricated and labeled as D1, D2, D3, D4 and D5, respectively.

Gas sensing properties of the sensor were measured by a conventional static mounting method. With a Linear DC Power Supply (Gwinstek GPD-3303S) providing stable current, the Pt heater formed on the Al<sub>2</sub>O<sub>3</sub> substrate offers the working temperature for the sensor. The surface temperature of the device is measured by using the infrared radiation thermometer (Flur T250). The sample gases containing different NO<sub>2</sub> concentration were obtained by diluting 10000 ppm NO<sub>2</sub> with O<sub>2</sub> (21 vol. %) and N<sub>2</sub> (79 vol. %) under 10% relative humidity (RH). When the sensor was exposed to air or the sample gas, the difference of electric potentials (V) between the sensing and reference electrodes was measured with a digital electrometer (Rigol. DM3054) as a sensing signal and the results obtained were recorded with a computer connected to the electrometer [43].

As a mixed-potential-type sensor, the change of electric potential difference for the sensor is defined as the response:

$$\Delta V = V_g - V_a$$

where  $V_g$  was the electric potential (V) difference measured under a working circumstance (air with different concentration of NO<sub>2</sub>), while  $V_a$  was one in air. Then, the slope coefficient of response value to the logarithm of the concentration was defined as sensitivity:  $S = \frac{\delta \Delta V}{\delta \log c}$ .

The current-voltage (polarization) curves were measured by means of potentiodynamic method (Instrument corporation of Shanghai, China, CHI600 C) at a constant scan-rate of 2 mV/min using a two-electrode configuration in the base gas (21 vol.% O<sub>2</sub> + N<sub>2</sub> balance) and the sample gas (100 ppm NO<sub>2</sub> + 21 vol.% O<sub>2</sub> + N<sub>2</sub> balance). The current axis of the anodic polarization curve was subtracted from that of the cathodic polarization curve at each potential so as to obtain the modified polarization curve in which the current axis is shown in absolute scale.

The complex impedance of the sensor in sample gas was measured by means of an impedance analyzer (Solartron, 1260 and Solartron, 1287) in the frequency range of 1 Hz–1 MHz. The amplitude of the ac potential signal was fixed at 50 mV in all measurements.

## 3. Results and discussion

### 3.1. Thermal analysis of MnCr<sub>2</sub>O<sub>4</sub> gel

During the calcinations process, the organic species are released from the matrix and decomposed, along with the formation of oxide phase at corresponding crystallization and growth temperatures. Fig. 1 shows the TG-DSC curve of the gel. Four main weight loss processes have been observed from Fig. 1. First, in the range from the room temperature to 150 °C, slight weight loss was seen, accompanied with endothermic behavior. The endothermic peak at about 90 °C can mainly be attributed to desorption or release of some substances included in the gel, such as physically adsorbed water. Then a greatly intensity of weight loss was observed in the range from 150 to 200 °C. At the same time, there are two minor endothermic peaks around 150 and 190 °C, which can be related to the melt and release of the organic molecules. In next range of 200–400 °C, a large weight loss exists, accompanied with the largest exothermic peak which could be assigned to the collapse of gel network and combustions of most of the organic materials. As shown in the inset of Fig. 1, the weight loss is tiny after 400 °C, which is mainly caused by desorption of residual hydroxyl group [44]. During this temperature range, some tiny exothermic steps which can be attributed to the gradual crystallization of MnCr<sub>2</sub>O<sub>4</sub> can be seen.

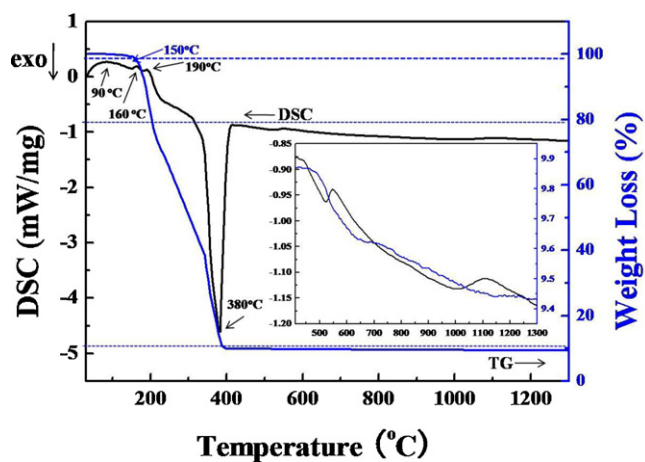


Fig. 1. TG-DSC curve of the gel of  $\text{MnCr}_2\text{O}_4$ , inset is the enlarged view in the range of 410 to 1300 °C.

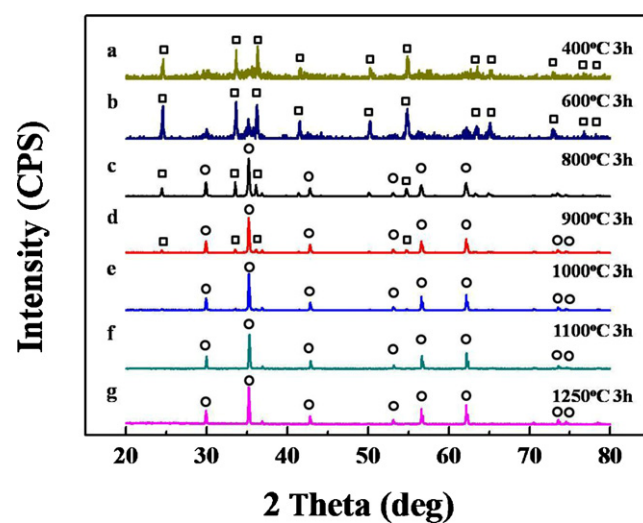


Fig. 2. XRD patterns of  $\text{MnCr}_2\text{O}_4$  nanoparticles calcined at different temperatures. (□)  $\text{Cr}_2\text{O}_3$ , (○)  $\text{MnCr}_2\text{O}_4$ .

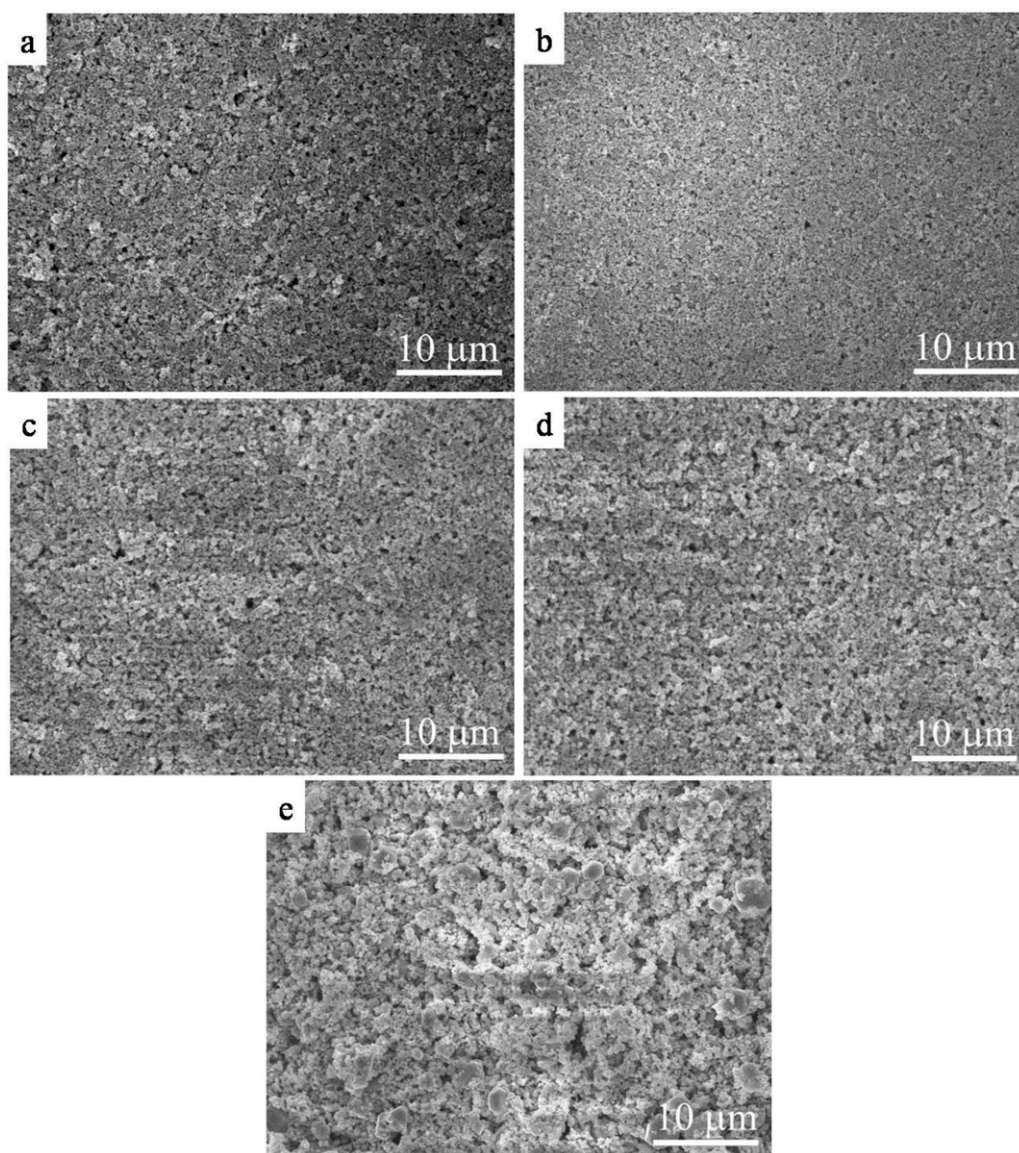


Fig. 3. SEM images of sensing electrodes with  $\text{MnCr}_2\text{O}_4$  calcined at different temperatures: (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C and (e) 1250 °C.



**Table 1**BET surface areas ( $S_{\text{BET}}$ ) vs. calcinations temperature for  $\text{MnCr}_2\text{O}_4$ .

|                                            |       |      |     |     |      |      |      |
|--------------------------------------------|-------|------|-----|-----|------|------|------|
| T (°C)                                     | 400   | 600  | 800 | 900 | 1000 | 1100 | 1250 |
| $S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ ) | 149.0 | 21.8 | 9.0 | 7.0 | 4.9  | 4.5  | 4.0  |

### 3.2. Crystal-phase composition of $\text{MnCr}_2\text{O}_4$ nanoparticles and BET analysis

X-ray diffraction patterns of the samples sintered at different temperature are shown in Fig. 2. When the dried gel was sintered at 400 °C, as shown in Fig. 2 (a), the  $\text{Cr}_2\text{O}_3$  with rhombohedral structure is dominant against the  $\text{MnCr}_2\text{O}_4$  and  $\text{MnO}$  with cubic structure. However, with increasing the sintering temperature, the peaks of  $\text{Cr}_2\text{O}_3$  and  $\text{MnO}$  became weaker, while the peaks of  $\text{MnCr}_2\text{O}_4$  were strengthened. When the sintering temperature is higher than 1000 °C, almost pure  $\text{MnCr}_2\text{O}_4$  with spinel structure was obtained.

The BET surface areas of the samples calcined at different temperatures are shown in Table 1. The sample sintered at 400 °C give the largest specific surface area, which is rationalized that the organic ingredients have not completely removed. For the sample calcined at 600 °C, the BET surface areas were reduced to 21.8  $\text{m}^2/\text{g}$ . When sintered at higher temperature, the specific surface area slowly decreases with increasing sintering temperature, which can be attributed to melt and re-crystallization of the material. This is consistent with the results described in the TG-DSC analysis.

### 3.3. Morphology of sensing electrodes of $\text{MnCr}_2\text{O}_4$ calcined at different temperatures

SEM images of the sensing electrodes (SEs) with aforementioned oxides calcined at 800, 900, 1000, 1100 and 1250 °C are shown in Fig. 3a–e. The sensing electrodes were sintered at 800 °C. Although the agglomerates of the particles are observed in all the images, the growth of the particles can be clearly seen with increasing the sintering temperature. The evolution of the sample morphology with increasing the sintering temperature can be explained as follow: After sintering at 400 °C, the polymer in the gel was removed and the oxide particles were left; then, as the temperature was sequentially elevated, the oxide particles became sintering with different degree, leading to the different degree agglomerates of the particles and tense surfaces morphology. When the sintering temperature was further increased, the particles of the oxides continue to grow and induced a porous surface morphology.

### 3.4. $\text{NO}_2$ sensing properties

Fig. 4 shows the influence of sintering temperature on the response of  $\text{MnCr}_2\text{O}_4$ -based sensors to 100 ppm  $\text{NO}_2$  at an operating temperature of 650 °C. Among the samples sintered at different temperatures, the sample calcined at 1000 °C showed the largest response, the response value to 100 ppm  $\text{NO}_2$  was about 73 mV. So, much attention was paid to the sensor based on  $\text{MnCr}_2\text{O}_4$  sintered at 1000 °C (Sensor D3).

Fig. 5a shows the continuous response and recovery transients to 5–600 ppm  $\text{NO}_2$  for Sensor D3 at 650 °C. Both at the low and high concentrations the response and recovery speeds are fast; and the dependence of the  $\Delta V$  on  $\text{NO}_2$  concentrations is shown in Fig. 5b, from which we can find the excellent linear relationship that is usually observed in mixed-potential-type sensors.

The cross-sensitivities to various gases for the Sensor D3 are exhibited in Fig. 6. It is seen that the present sensor exhibits rather high selectivity to  $\text{NO}_2$ : the  $\Delta V$  to  $\text{NO}_2$  is more than 70 mV, whereas the  $|\Delta V|$  values to the other gases are less than 10 mV. Even to

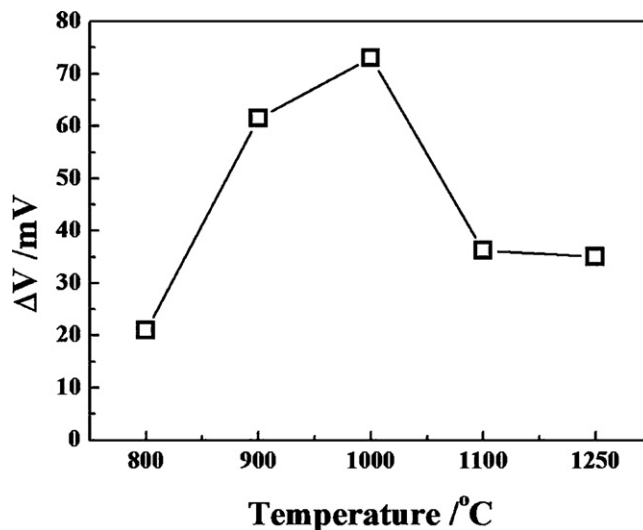


Fig. 4. Response to 100 ppm  $\text{NO}_2$  of sensors based on  $\text{MnCr}_2\text{O}_4$  calcined at different temperatures.

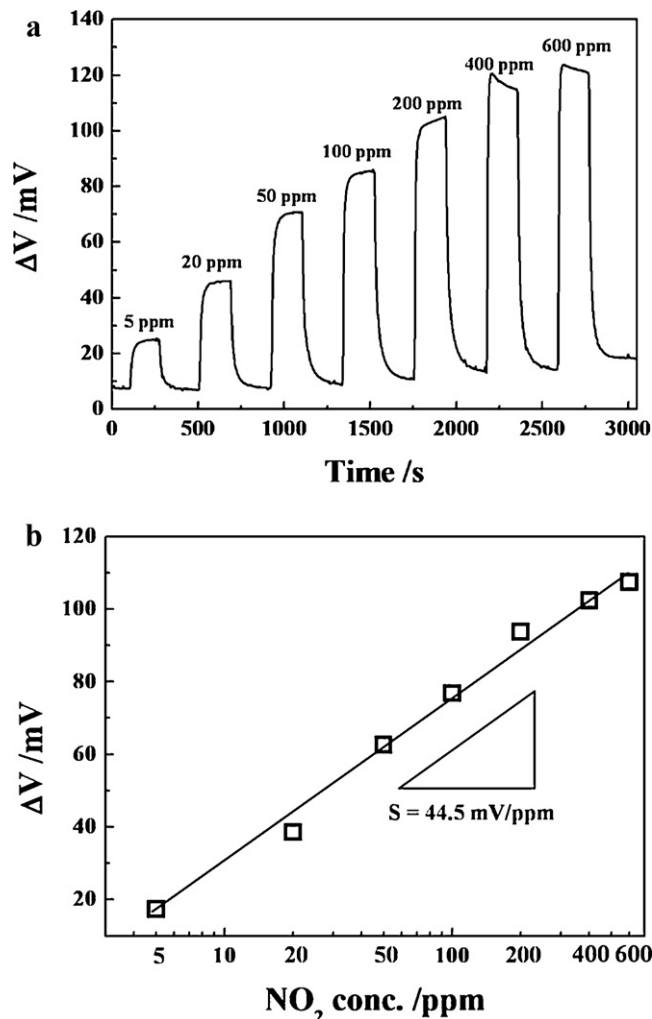


Fig. 5. (a) Normalized curve of responses of sensor D3 to different concentrations of  $\text{NO}_2$  at 650 °C under the wet condition. (b) Dependence of the  $\Delta V$  on concentrations of sensor D3 under the wet condition.

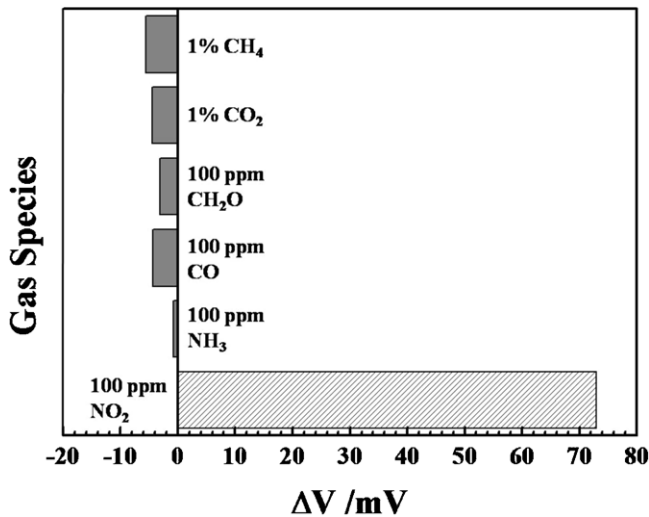


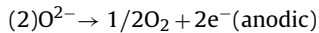
Fig. 6. Cross-sensitivities to various gases for D3 at 650 °C under the wet condition.

1000 ppm  $\text{CH}_4$  and  $\text{CO}_2$ , the Sensor D3 also gives a rather low response value.

The present device was subjected to additional test, in which, it exposed to 100 ppm  $\text{NO}_2$  repeated seven times at 650 °C. As shown in Fig. 7, the voltage response to 100 ppm  $\text{NO}_2$  and air reproduce very well in 7-time cycles examined. This result confirms that the reproducibility of the voltage response of the device is rather good.

### 3.5. Sensing mechanism of the mixed-potential-type $\text{NO}_2$ sensors

The sensing behavior of the potentiometric  $\text{NO}_2$  sensor using YSZ and the oxide electrode has been explained by the mixed potential mechanism [45]. The response is generated by two electrochemical semireactions that take place at same time on the SE in  $\text{O}_2$ -containing atmosphere as follow:



These semireactions compete at the SE/YSZ interface: either promoting semireaction (1) or restraining semireaction (2) will improve the potential of SE. To rationalize that, the polarization curves were obtained in air and in the sample gas ( $\text{NO}_2$  + air) using the method reported previously [46]. Fig. 8 shows the modified polarization curves for the sensors attached with each of 900, 1000

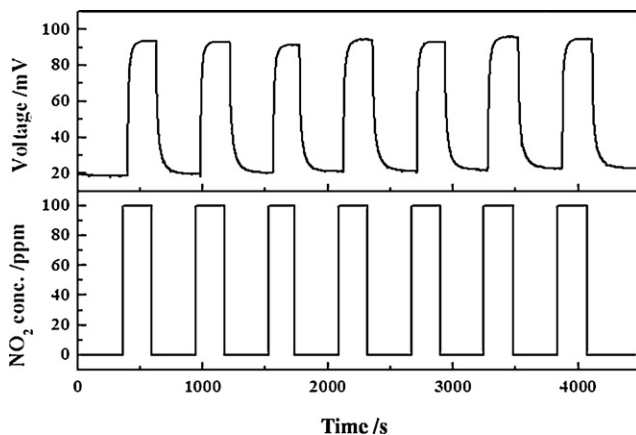


Fig. 7. Repeated response transients of the sensor D3 upon switching on- and off-  $\text{NO}_2$  repeatedly at 650 °C under the wet condition.

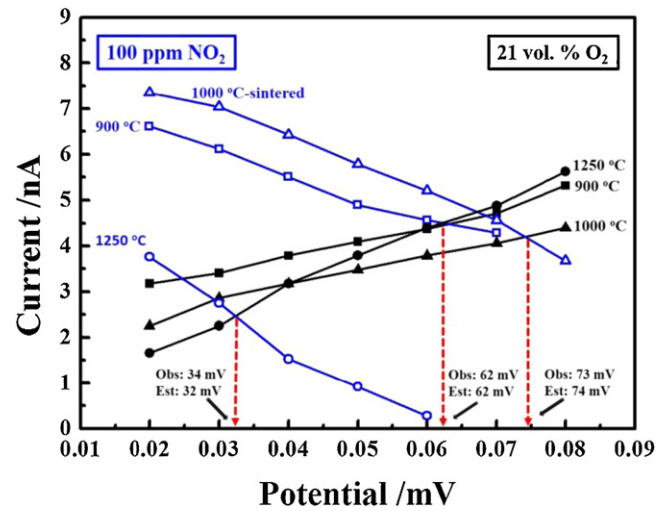


Fig. 8. Modified-polarization curves in 21 vol.%  $\text{O}_2$  and 100 ppm  $\text{NO}_2$  for the planar sensor attached with  $\text{MnCr}_2\text{O}_4$  sintered at 900, 1000 and 1250 °C.

and 1250 °C-sintered  $\text{MnCr}_2\text{O}_4$ -SEs. It can be seen that the sensor attached with 1000 °C-sintered  $\text{MnCr}_2\text{O}_4$ -SE shows the increased catalytic activity for electrochemical reaction (1) and decreased for reaction (2), resulting in a largest potential value. Additionally, the intersecting-potential values are very similar to those obtained, which confirms that the present sensors are operating under the mixed-potential mechanism [36].

Nyquist plots measured in the sample gas (100 ppm + air) at 650 °C under humid conditions for sensors using the  $\text{MnCr}_2\text{O}_4$ -SEs calcined at 900, 1000 and 1250 °C were shown in the Fig. 9. In the low frequency range, the interfacial resistance is large and changes with the calcination temperature. As reported previously [47], the total resistance of the sensors seems to be affected by the interfacial resistance between the SE material and YSZ. The factor about triple phase boundary should be taken into consideration, for it is the place where the electrochemical reactions occur. Therefore, the microstructure of the SE cannot be ignored, since it affects the area of the triple phase boundary. As shown in Scheme 2, comparing the local scheme (a) and (b), we can find that the interface of the particles of SE material and the YSZ increases with the particles enlarge but the triple phase boundary (the contacted position of the interface and gas) reduces.

As described above, with increasing the elevated temperatures, at first, the crystallization of the  $\text{MnCr}_2\text{O}_4$  plays an important role

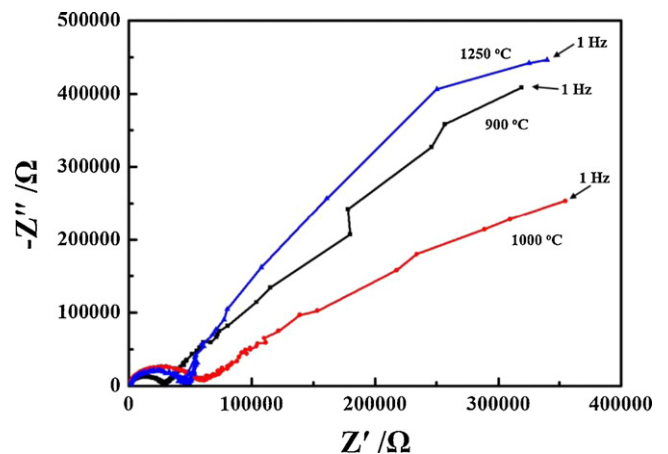
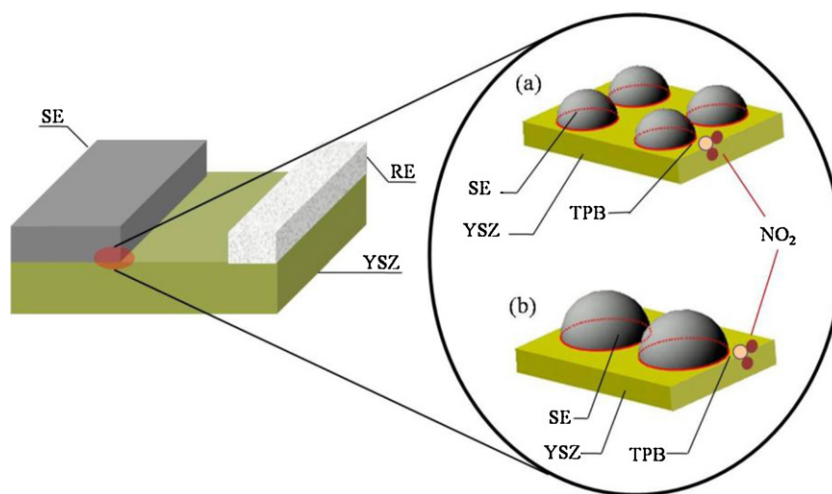


Fig. 9. Nyquist plots of the planar sensor attached with  $\text{MnCr}_2\text{O}_4$  sintered at 900, 1000 and 1250 °C, examined in 100 ppm  $\text{NO}_2$  (21 vol.%  $\text{O}_2$ ).



**Scheme 2.** Schematic representation of the sensor electrodes and the local schema: the local TPB with different size particles of sensing material is shown in (a) and (b).

on the response, for it affects the electrochemical activity, and results in the increasing response value (below 1000 °C). However, we can see that the crystallite enlarges and the surface area decreases with the further increase of annealing temperature. Then, the microstructure should be taken into account: the enlarged crystal size reduces the area of the triple phase boundary, and the reduced area brings about the decreased response value (after 1000 °C). Obviously, with increasing the calcined temperature, the crystalline quality and the microstructure of the SE material changed, and both of them affect the variation of the NO<sub>2</sub> response of MnCr<sub>2</sub>O<sub>4</sub>.

#### 4. Conclusion

The results show that the sintering temperatures affect the crystallization of MnCr<sub>2</sub>O<sub>4</sub> nanoparticles, confirming the thermal stability of the synthesized material by TG-DSC, XRD, BET and SEM. Sensors combining YSZ-plate with MnCr<sub>2</sub>O<sub>4</sub> calcined at different temperature (800, 900, 1000, 1100 and 1250 °C) were fabricated and tested. The result reveals that the sensor using the material calcined at 1000 °C exhibits optimal response to NO<sub>2</sub>. Further tests were taken with a concentration range of 5 to 600 ppm, and agree with the linear relationship between the response and logarithm of the concentration. The selectivity and repetitiveness tests have been taken and the results are good. As discussed in the sensing mechanism, it was suggested that when temperature increased, a rather pure MnCr<sub>2</sub>O<sub>4</sub> phase was obtained after 1000 °C; however, taking account of the triple phase boundary, a high surface area is necessary, so too high temperature is not good for it. These two factors determined 1000 °C as the optimal temperature.

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